The effect of pressure on the rate of the benzidine rearrangement III : 2,2'-dibromohydrazobenzene

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THE EFFECT OF PRESSURE ON THE RATE OF THE BENZIDINE REARRANGEMENT III

2,2'-Dibromohydrazobenzene

BY JIRO OSUGI, MUNEO SASAKI AND ICHIRO ONISHI

The rates of the acid-catalysed rearrangement of 2,2'-dibromohydrazobenzene in aqueous ethanol (85 vol% EtOH) have been measured at pressures up to 3,000 kg/cm^2.

It was observed that two different reaction: one is of first order with respect to [HCl] (one-proton mechanism), and the other is of second order (two-proton mechanism), occurred concurrently and the former was strongly accelerated by pressure.

From the values of volumes, energies and entropies of activation: $\Delta V_1^{\neq}=-10.7$ cc/mole, $E_1^{\neq}=16.3$ kcal/mole, $\Delta S_1^{\neq}=-34$ e.u. for the one-proton mechanism and $\Delta V_2^{\neq}=-0.4$ cc/mole, $E_2^{\neq}=29$ kcal/mole, $\Delta S_2^{\neq}=7.3$ e.u. for the two-proton mechamism, the transition states of the both mechanisms were discussed.

Introduction

As one of a series of studies[1) 2)] of the pressure effect on the rate of the benzidine rearrangement of hydrazocompounds, it has been reported in the previous paper that in the case of 2,2-hydrazotoluene the rearrangement took place through one- and two-proton mechanisms concurrently, in contrast to only the two-proton mechanism in the case of hydrazobenzene and that the protonation steps are both in the pre-equilibria.

A part of this change of the mechanism was attributed to the heterolytic charge separation due to the substituent[2) 3)]. From these viewpoints of substituent effects, the author studied the effect of pressure on the rate of rearrangement of 2,2'-dibromohydrazobenzene having electro-attractive group.

Experiment

Materials

G.R. grade reagents of 99.5 vol% ethanol, hydrochloric acid and lithium chloride were used. 2,2'-Dibromohydrazobenzene (B) was synthesized by Snyder's method[4)] and recrystallized from petroleum

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2) J. Osugi, M. Sasaki and I. Onishi, *ibid.*, **36**, 100 (1966)
3) D. V. Banthorpe, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, **1964** 2864
4) H. R. Snyder, C. Weaver and C. Marshall, *J. Am. Chem. Soc.*, **71**, 289 (1949)

ether to get white crystal melting at 98°C. 3,3-Dibromobenzidine (P) was synthesized by shaking the etherial solution of (B) with cold concentrated hydrochloric acid and recrystallized from ethanol to get white solid melting at 127°C. 2,2′-Dibromoazobenzene (A) was synthesized by the oxidation of the alkaline ethanolic solution of (B) with air, separated with thin-layer chromatography and recrystallized from ethanol to get orange crystal melting at 132°C.

Table 1 Elementary analysis of 2,2′-dibromoazobenzene (A)

	Calc.	Found
C	42.39	42.42
H	2.37	2.24
N	8.24	8.50
Br	47.00	47.07

Procedure

The reaction medium was prepared by mixing two solutions : one of which is a mixture of 99.5 vol% ethanol and concentrated hydrochloric acid and the other is a mixture of 99.5 vol% ethanol and aqueous solution of lithium chloride. The concentrations of the components of each medium were controlled so as to give the available concentrations after mixing, *i.e.* for ethanol, 85 vol%, and for hydrochloric acid and ionic strength the fixed values considering the compressibility of aqueous ethanol, under the condition of both atmospheric and high pressures. A high pressure apparatus used for this work was the same as previously reported. Keeping the reaction medium in a thermostat at constant temperature, a scanty amount of 2,2′-dibromohydrazobenzene (B) was added, and the initial concentration of (B) was estimated to be about 2×10^{-4} mole/l. In the case of high pressure experiment, a glass syringe containing 1.0 ml of the reaction solution was put into the cylindrical pressure vessel, and the reaction temperature was kept constant by allowing the thermostatted water to circulate around the high pressure vessel and was measured by an iron-constantan thermocouple. As soon as the available pressure was reached, an aliquot of the same solution which had been stored in the thermostat was diluted to the desired concentration, and the initial concentrations of (B), (A) and (P) were determined from the absorbances at 245, 285 and 320 mμ. After an appropriate reaction time

Table 2 Molecular extinction coefficients ($\varepsilon\times10^{-3}$) at μ=0.178N

	[HCl] (N)	245 mμ	285 mμ	320 mμ
2,2′-Dibromohydrazobenzene		19.5	4.57	0.17
2,2′-Dibromoazobenzene		10.1	5.66	12.0
3,3-Dibromobenzidine	0.178	12.4	8.32	5.57
	0.142	11.4	9.56	6.65
	0.107	10.14	11.0	8.04
	0.071	8.76	12.9	9.65
	0.0533	7.83	13.9	10.55
	0.0355	6.81	15.1	11.50

The Review of Physical Chemistry of Japan Vol. 39 No. 1 (1969)

interval, pressure was withdrawn and each component in the reaction mixture was analyzed in the same way. The measurements were performed up to 3,000 kg/cm^2 in the temperature range, 25°~40°C.

The values of the molecular extinction coefficients used for analysis are shown in Table 2, where the values for (P) vary with the concentrations of hydrochloric acid in ethanol.

Results

In this study both the acid-catalysed rearrangement and the oxidation reaction proceeded concurrently in the presence of dissolved oxygen. But, as the sum of each concentration of (B), (P) and (A) was maintained constant until the concentration of (B) decreased to one-tenth of the initial within the error of $\pm 1\%$, and good linearity in Fig. 1 was obtained, it seems likely that the disproportionation reaction does not occur. The result is inconsistent with that of Ingold's[5], where the formation of small quantity of o-bromoaniline was reported.

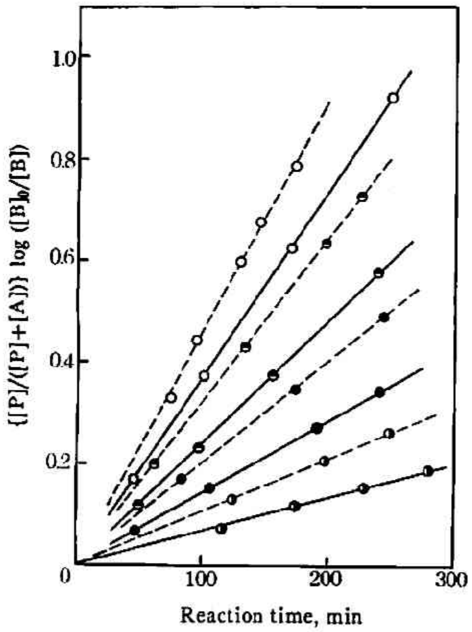


Fig. 1 First order plot (40°C, μ=1.78)
Pressure (kg/cm^2); —— 1, --- 3,000.
[HCl] (mole/l); ○: 1.78, ◓: 1.42, ●: 1.07, ◑: 0.71.

As the overall rate of disappearance of (B) is of first order for (B), the apparent rate constant of rearrangement, k_r, and that of the oxidation, k_{ox}, were obtained by dividing the overall first order rate constant of the decrease of (B), into the ratios of [P] and [A].

$$-\mathrm{d}[B]/\mathrm{d}t = (k_r + k_{ox})[B] \tag{1}$$

$$\frac{[P]}{[P]+[A]} \ln \frac{[B]_0}{[B]} = k_r\, t \tag{1'}$$

In the case of ionic strength, μ=1.78, the curve shown in Fig. 2 was obtained by plotting log k_r

5) D. V. Banthorpe, C. K. Ingold and M. O. Sullivan, *J. Chem. Soc.*, **1968B**, 624

against log [HCl], the slope of which increased from 1.6 to 1.9 with acidity. The non-integral order which increases with acidity indicates the fact that two different reactions take place. And the plots of k_r/[HCl] against [HCl] give straight lines as shown in Fig. 3. The result is expressed by the following equation.

$$k_r/[\mathrm{HCl}] = k_1 + k_2[\mathrm{HCl}]. \qquad (2)$$

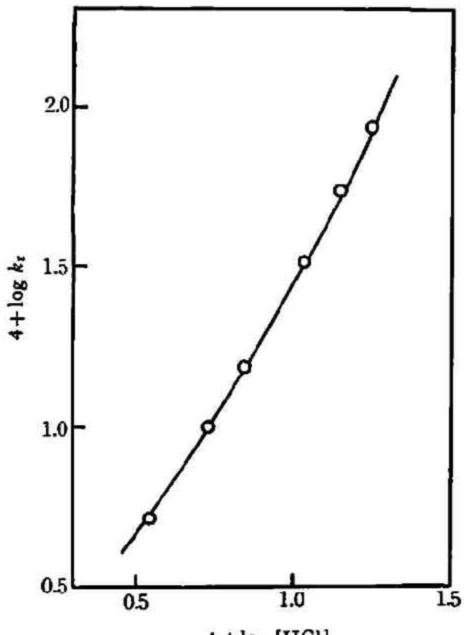


Fig. 2 Plot of logarithms of apparent first order rate constants against those of [HCl], 40°C, 1 kg/cm², μ=1.78 in 85 vol% EtOH

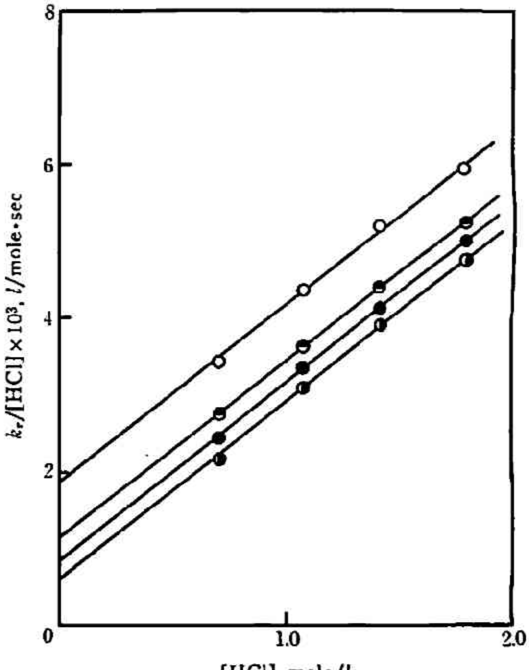


Fig. 3 Relationship between the apparent first order rate constants of rearrangement and [HCl] (40°C)
Pressure (kg/cm²);
◐: 1, ●: 1,000, ◒: 2,000,
○: 3,000

From Fig. 3 the rate constant k_1 of the one-proton mechanism (the first order for [HCl]) and the rate constant of k_2 of the two-proton mechanism (the second order for [HCl]) can be obtained, and these values are summarized in Table 3.

Fig. 5 illustrates the plots of $\log(k^P/k^1)$ against P for k_1 and k_2, where k^1 and k^P are the rate constants at atmospheric pressure and at P kg/cm², respectively. From the slopes of these lines and equation (3), the volumes of activation of the one-proton mechanism, $\Delta V_1^{\ddagger}$, and that of the two-proton one, $\Delta V_2^{\ddagger}$, were calculated.

$$-\frac{\partial \ln (k^P/k^1)}{\partial P} = \frac{\Delta V^{\ddagger}}{RT}. \qquad (3)$$

Further, the energies of activation $E_1^{\ddagger}$, $E_2^{\ddagger}$ and the entropies of activation $\Delta S_1^{\ddagger}$, $\Delta S_2^{\ddagger}$, were

Table 3 Rate constants for the rearrangement (μ=1.78)

Temp. (°C)	Pressure (kg/cm²)	$k_1 \times 10^3$ ($l \cdot mole^{-1} \cdot min^{-1}$)	$k_2 \times 10^3$ ($l^2 \cdot mole^{-2} \cdot min^{-1}$)
40	1	0.60	2.36
40	1,000	0.84	2.36
40	2,000	1.19	2.30
40	3,000	1.83	2.33
35	1	0.40	1.12
30	1	0.25	0.48
30	2,000	0.54	0.49
30	3,000	0.84	0.51
25	1	0.16	0.23
25	3,000	0.60	0.24

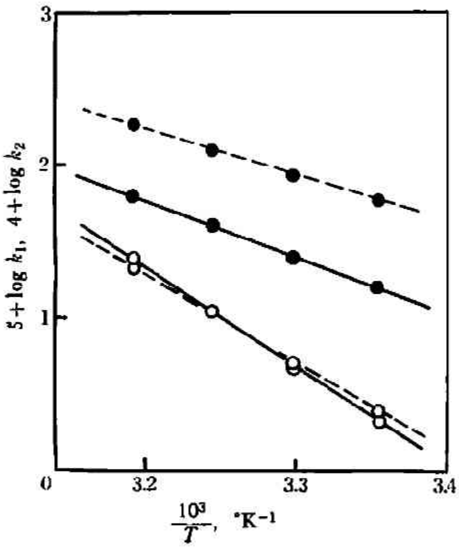


Fig. 4 Dependence of the rates of the rearrangement on temperature

—●— k_1, 1 kg/cm²
---●--- k_1, 3,000 kg/cm²
—○— k_2, 1 kg/cm²
---○--- k_2, 3,000 kg/cm²

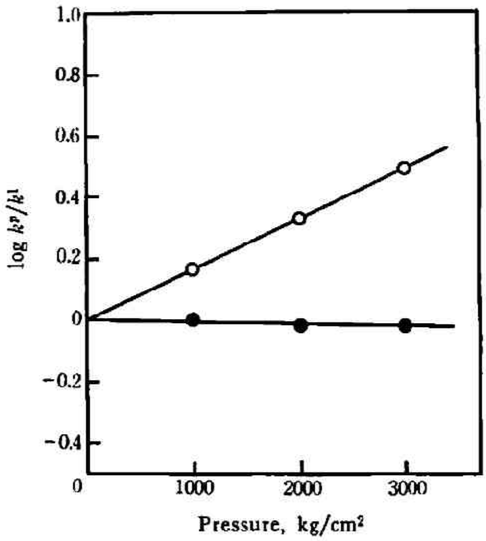


Fig. 5 Dependence of the rates of the rearrangement on pressure (40°C)

○: k_1, ●: k_2

Table 4 Kinetic data for rearrangement

	Press. kg/cm²	One-proton $\Delta V_1^{\ne}$ cc/mole	One-proton $E_1^{\ne}$ kcal/mole	One-proton $\Delta S_1^{\ne}$ e.u.	Two-proton $\Delta V_2^{\ne}$ cc/mole	Two-proton $E_2^{\ne}$ kcal/mole	Two-proton $\Delta S_2^{\ne}$ e.u.
Hydrazobenzene[1)]	1	—	—	—	1.5	20.7	3.6
	3,000					19.0	−2.4
2,2'-Dimethylhydrazobenzene[2)]	1	−2.5	20.9	0.6	−7.2	21.0	4.1
	3,000		21.6	3.3		21.9	8.9
2,2'-Dibromohydrozobenzene	1	−10.7	16.3	−34	−0.4	29.0	7.3
	3,000		13.2	−41		28.2	4.8

Table 5 Variation of $\Delta V^{\ddagger}$ with temperature

Temp., °C	$\Delta V_1^{\ddagger}$, cc/mole	$\Delta V_2^{\ddagger}$, cc/mole
40	− 9.1	0.2
30	−10.0	−0.5
25	−10.7	−0.4

obtained at each pressure and these values are summarized on Tables 4 and 5 involving the results of the previous reports[1) 2)].

In the case of 2,2′-dibromohydrazobenzene, although the variation of $\Delta V_2^{\ddagger}$ seems to sink under the error, the mean temperature differential of $\Delta V_1^{\ddagger}$ and the mean pressure differential of $\Delta S_1^{\ddagger}$ were obtained as follows.

$$\Delta\Delta V_1^{\ddagger}/\Delta T = 0.104\ \mathrm{cm^3/mole{\cdot}deg} \tag{4}$$

$$-\Delta\Delta S_1^{\ddagger}/\Delta P = 0.106\ \mathrm{cm^3/mole{\cdot}deg} \tag{5}$$

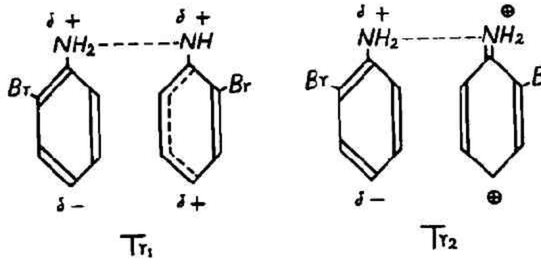
This relation shows that the following thermodynamic equation is approximately satisfied.

$$\left(\frac{\partial \Delta V_1^{\ddagger}}{\partial T}\right)_P = -\left(\frac{\partial \Delta S_1^{\ddagger}}{\partial P}\right)_T . \tag{6}$$

Discussion

In the case of 2,2′-dimethylhydrazobenzene reported previously, the separation of N : N bond and the distance between the two *para* positions were considered to be the same for two transition states, Tr_1 (for one-proton) and Tr_2 (for two-proton) under the assumption that two transition states have the similar form as postulated by Ingold[3)], and the difference between the volumes of activation of the two-proton and the one-proton mechanisms, $\Delta V_2^{\ddagger} - \Delta V_1^{\ddagger} = -4.7$ cc/mole, was explained to be

$$\begin{tikzcd}
B \arrow[r, shift left, "K\quad H^+"] & BH^+ \arrow[l, shift left] \arrow[r, shift left, "k'\quad H^+"] \arrow[d, "k_1^*"'] & BH_2^{++} \arrow[l, shift left, "k'_{-1}"] \arrow[d, "k_2^*"] \\
 & P & P
\end{tikzcd}$$



Tr₁ Tr₂

consistent with the volume change of protonation to aniline from H_3O^+, $\Delta\overline{V}^0 = -5.2$ cc/mole[6) 7)]. Therefore, it was concluded that the second proton transfer step was in a pre-equilibrium.

But in the present case of 2.2'-dibromohydrazobenzene, in view of the facts that the difference of the volume of activation is $\Delta V_2^{\neq} - \Delta V_1^{\neq} = 10.3$ cc/mole, and that the entropies of activation in the two mechanisms are considerably different, it does not seem likely that the second protonation is in a pre-equilibrium and that the reaction takes place through the same kind of transition states, Tr_1 and Tr_2. So it may be probable that the two transition states are different from each other, and/or the second proton transfer is a rate-determining step.

Ingold has described, according to his "polar transition state theory", that the electrostatic effects of base weakening of the substituent on the protonated aryl ring and of electron-releasing of the substituent on the non-protonated ring contributed to facilitating the one-proton mechanism without the second protonation.

The basicity constant of halogenoaniline cited from literature[8)] is summarized in Table 6.

Table 6 pK_b in 30% aqueous ethanol at 25°C

	H	F	Cl	Br	I
ortho	9.9	11.53	11.87	12.00	12.44
meta	9.9	10.87	11.07	11.10	11.12
para	9.9	9.92	10.54	10.66	10.82

In the case of 2.2'-dibromohydrazobenzene, the facts that the rate constant k_1 is 4,000 times smaller and k_2 is 13,000 times smaller than those of 2.2'-dimethylhydrazobenzene and that the rearrangement takes place according to both one- and two-proton mechanisms, can be attributed to the decrease of basicity. At the same time, it is probably implied that the second proton transfer is more unlikely.

Conclusively, the results that $\Delta V_1^{\neq} = -10.7$ cc/mole and $\Delta S_1^{\neq} = -34$ e.u. imply that the transition state of one-proton mechanism is more polar, rigid and solvated form. And from the values of $\Delta V_2^{\neq} = -0.4$ cc/mole and $\Delta S_2^{\neq} = 7.3$ e.u. for two-proton mechanism, it can be concluded that if the second proton transfer is in a pre-equilibrium, the transition state may be a long extended less polar one, and if the second protonation is a rate-determining, desolvation must be accompanied and the latter is well understood from the appreciably large value of the activation energy.

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7) S. D. Hamann and W. Strauss, *ibid.*, **51**, 1684 (1955)
8) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", p. 741, Cornell University Press, Ithaca, New York (1953)